



CONDITIONS FOR TRANSITION FROM BARRIER TO POROUS OXIDATION OF ALUMINUM IN PHOSPHORIC ACID SOLUTIONS



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ABSTRACT

Anodic oxidation of aluminum foil specimens in the phosphoric acid solutions of various concentrations was studied under the galvanostatic conditions at various current densities. The efficiency of barrier oxidation was determined by the slopes of linear portions of time dependence of voltage across the electrochemical cell electrodes. The SEM micrographs of oxidized specimens are presented. It was shown that the critical oxidation efficiency for the transition from the barrier oxidation to porous oxidation is equal to the reciprocal of the Pilling–Bedworth ratio (0.61). The power dependence of the rate of field assisted ejection of metal cations from oxide film on the current density was supported experimentally. The exponent of power function was found to be about 0.5.

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1. Introduction

Two types of anodic oxidation of metals can be recognized: the barrier oxidation and porous oxidation. Both types are of great practical importance. At present, the porous oxidation has more diversified applications. In contrast to the barrier oxidation, porous oxidation is performed in the solutions, where the oxide is moderately soluble. In the formation of porous anodic oxide films, at the first stage, the growth of barrier film takes place; at the second stage, it gives way to the porous oxide growth. This is due to the fact that, along with the growth of anodic oxide film, its dissolution occurs.

The mechanism of porous oxidation was considered by many authors, for example [1–7]. It was found that, under certain conditions, the barrier oxidation loses its stability. The current is focused on some areas. On these areas, the dissolution of AOF is accelerated leading to the pore initiation. The transition to the quasi-steady-state porous oxidation takes place. The transfer of oxygen ions in the AOF towards the boundary with metal and the motion of metal ions in the opposite direction in the spherical barrier oxide layer on the pore bottom proceed via their motion in a strong electric field. Thereby, the rate of barrier layer dissolution on

the pore bottom (at the outer boundary) is equal to the rate of its formation at the inner boundary (the oxide/metal interface). This rate is 100–1000 nm/min [5]; it is by 4–5 orders higher than the rate of chemical dissolution of pore walls oxide leading to their widening from the bottom to the surface. In different works, extremely high-rate dissolution of barrier layer in the course of its growth in strong electric field was considered as the field assisted dissolution or field assisted cation ejection (FACE). According to different authors, this phenomenon can be caused by the local overheating [6], acidification of solution as a result of oxide formation [8], and weakening of metal–oxygen bond under the action of electric field [3].

The mechanism of high-rate dissolution of barrier layer in strong electric field was proposed in [9]. It is based on the Vetter's concept that the transition of metal cations from the oxide surface to the solution is the slow stage of oxide dissolution [10]. The acceleration of oxide dissolution during its anodic formation is explained in [9] by considerable weakening of the bond of those metal ions in the oxide, which are in contact with the electrolyte, when oxygen vacancies approach them. The approach of oxygen vacancy to the surface metal ions means the breakdown of one bond between the metal ion and oxygen in the oxide. A probability of transition of metal ion, neighboring to the oxygen vacancy or interstitial metal ion, to the solution is much higher than that of another metal ion.

From the theory of AOF growth in strong fields [11], it follows that the number of ionic current carriers and the rate of their

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motion exponentially increase with increasing strength of electric field. The ionic current density, which is proportional to the product of the number of ionic current carriers and the rate of their motion, also exponentially increases with increasing field strength. From [11] it follows that the concentration of ionic carriers, in particular, the concentration of oxygen vacancies and interstitial metal ions in AOF, is a power function of the current density. If the FACE rate is proportional to the concentration of ionic carriers in the AOF, the rate of field accelerated dissolution V_{FACE} is a power function of the current density i : $V_{\text{FACE}} = k_1 i^b$, where b is the exponent of power function, $0 < b < 1$. This raises the question of the value of b .

The transition from the barrier oxidation to the porous oxidation takes place due to the loss of oxidation front stability when the oxidation efficiency (a ratio of amount of oxide, which is retained in the AOF, to the total amount of formed metal oxide) decreases below the critical value f_c .

The authors of [12,13] suppose that the transition to the porous oxidation takes place, when all Al^{3+} ions, which are transferred by the ionic current in the oxide, pass to the solution. Taking the oxygen transfer number to be 0.6, they obtained $f_c = 0.6$ [13]. However, their experiments [12] showed that the porous films grow also at the oxidation efficiency above 0.9. (It should be noted that the data are compared with the efficiency of porous oxidation.) The authors explain this fact by the effect of oxide flow in the barrier part of the film [14–16].

The authors of [17] proposed that the critical oxidation efficiency f_c is determined as $f_c = (\text{PBR})^{-1}$, where (PBR) is the Pilling–Bedworth ratio [18], which is the ratio of oxide volume to the volume of metal, from which the oxide was produced. The authors of [18] assumed that all metal atoms remain in the oxide. As applied to the anodic metal oxidation, these considerations should be corrected for the dissolution of a fraction of atoms in the electrolyte, so the volume of formed oxide is by f times smaller, and the criterion of front stability is

$f \times \text{PBR} > 1$. Consequently, the critical efficiency is equal to $(\text{PBR})^{-1}$.

Hebert et al. [19] briefly considered the instability mechanisms during anodic film growth. They presented a linear stability analysis of an instability mechanism controlled by oxide dissolution and ion migration. In their model of anodic films, metal and oxygen ions move independently, but their fluxes are coupled through the constraint of volume conservation at the metal/oxide

interface. In their model, as well as in [17], the oxidation efficiency and (PBR) are the most important parameters, which determine the oxidation front stability.

It should be emphasized that the transition from the barrier oxidation to porous one is irreversible, i.e. the conditions of the transition from the porous oxidation to barrier one differ essentially from those for the transition from the barrier oxidation to porous one. This means that the oxidation efficiency refers to the barrier oxidation.

In this work, the earlier proposed hypothesis [17] will be checked experimentally for a particular case of aluminum oxidation in the dilute aqueous solutions of phosphoric acid.

2. Experimental procedure

In the experiments, a two-electrode cell of volume 250 ml with Al (99.99%) anode and titanium cathode was used. All experiments were performed at a temperature of 25 ± 0.5 °C; the solution was stirred with a magnetic stirrer. The power source was used to maintain a constant current to an accuracy of $\pm 0.2\%$. The voltage was recorded at intervals of 2 to 30 s. The foil specimens 100 μm thick measuring 10 by 20 mm were etched in 10% NaOH solution at a temperature of 50–60 °C for 2 min, electrochemically polished in 75% H_3PO_4 at a temperature of 70 °C for 3 min, washed in the distilled water, and dried in a dry warm air flow.

The concentration range of studied acid solutions was chosen so that at the lowest concentration, obviously barrier oxidation took place, and at the highest oxidation, obviously porous oxidation occurred. The linearity of the voltage vs. time curve and the absence of pores on the surface at a magnification of $\times 200000$ are the indications of the barrier oxidation. A specific shape of the voltage vs. time curve with a voltage peak and the presence of pores on the surface are the indications of evidently porous oxidation.

The surface morphology after the oxidation was examined by the micrographs that were obtained with a SUPRA 55VP-25-75 scanning electron microscope at a $\times 200$ to $\times 200000$ magnification.

The experiments were performed in 0.03 M phosphoric acid solution neutralized by ammonia to pH 6–7 and in phosphoric acid solution of various concentrations.

3. Determination of oxidation efficiency

The oxidation efficiency was determined by a slope b of voltage vs. time curves in the experiments of galvanostatic oxidation of pure aluminum (99.99%) foil specimens. The electronic conductivity of AOF on pure aluminum is negligibly low; therefore, in the electrolyte, where the oxide is insoluble (for example, 0.03 M phosphoric acid solution neutralized by ammonia to pH 6–7 is such an electrolyte), the entire measured current is consumed only by the growth of barrier AOF. In this case,

$$d\delta/dt = \gamma i, \quad (1)$$

where δ is the thickness of barrier AOF (cm), t is the time (s), γ is the volume electrochemical equivalent of aluminum oxide (cm^3/C), and i is the current density (A/cm^2).

Under the galvanostatic conditions, the components of voltage in the cell: the ohmic voltage in the electrolyte, the cathodic potential, and potential differences at the AOF/electrolyte and AOF/metal interfaces are constant; only the voltage drop on the AOF varies with time. Therefore, at $f = 1$, a slope of the voltage vs. time curve is

$$b_0 = dU/dt = \varepsilon \gamma i, \quad (2)$$

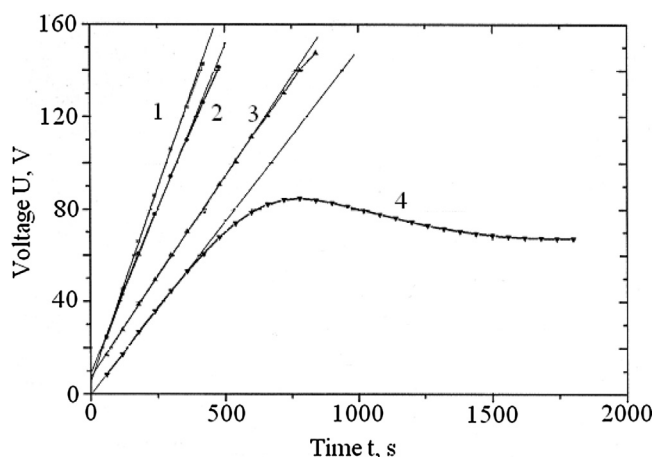


Fig. 1. Time dependences of voltage under the galvanostatic conditions in the solutions of various compositions: (1) 0.03 M $(\text{NH}_4)_2\text{HPO}_4$, pH 6–7; (2) 0.005 M H_3PO_4 ; (3) 0.030 M H_3PO_4 ; (4) 0.050 M H_3PO_4 . Temperature 25 °C, current density 0.95 mA/cm^2 .

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